REPORT DOCUMENTATION PAGE		Form Approved OMB NO. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 24-04-2014	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 18-Sep-2013 - 17-Mar-2014

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
W911NF-13-P-0021 / A13A-011-0305 Final Report Staib Instruments, Inc. Chemical Analyzer System for In Situ and Real Time Surface Monitoring	5b. GRANT NUMBER W911NF-13-P-0021
	5c. PROGRAM ELEMENT NUMBER 665502

6. AUTHORS Staib, Belenky, Shterengas, Calley, Kipshidze	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Staib Instruments, Inc. 101 Stafford Court Williamsburg, VA 23185 -5767	8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 64397-MS-ST1.1

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
The Phase 1 project to test the feasibility of Auger monitoring during MBE growth both in situ and real-time has resulted in a wealth of spectra to analyze. The equipment performs dependably without impacting the MBE process. The Auger spectra reproducibly track expected growth events while adding insight to dynamic surface conditions previously not observable. The data processing developed provides sufficient information for evaluations needed for Phase 1 feasibility studies.
As a result of the Phase 1 work, it has been shown that the Auger Probe is viable as an in situ real time chemical

15. SUBJECT TERMS
Auger, MBE Growth

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Philippe Staib
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	UU		19b. TELEPHONE NUMBER 757-565-7000

W911NF-13-P-0021 / A13A-011-0305
Final Report
Staib Instruments, Inc.
Chemical Analyzer System for In Situ and Real Time Surface Monitoring

ABSTRACT

The Phase 1 project to test the feasibility of Auger monitoring during MBE growth both in situ and real-time has resulted in a wealth of spectra to analyze. The equipment performs dependably without impacting the MBE process. The Auger spectra reproducibly track expected growth events while adding insight to dynamic surface conditions previously not observable. The data processing developed provides sufficient information for evaluations needed for Phase 1 feasibility studies.

As a result of the Phase 1 work, it has been shown that the Auger Probe is viable as an in situ real-time chemical monitoring tool for MBE. Such information can already be used to guide the growth process of materials for which the actual surface conditions are critical. Additionally, no limitations were noted that would prevent the use of the Probe for materials beyond those tested or in other growth methods, like PLD. The Auger Probe, after improvements and software updates for real time, continuous, multiple line acquisition, would prove to be a well suited tool for the characterization of in situ growth.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>   <u>Paper</u>

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>   <u>Paper</u>

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received   Paper

TOTAL:

Number of Manuscripts:

Books

Received   Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Ding Wang	0.30	
FTE Equivalent:	**0.30**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Ding Wang	0.30
FTE Equivalent:	**0.30**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Gela Kipshidze	0.40	
Leon Shterengas	0.04	No
Gregory Belenky	0.04	No
FTE Equivalent:	**0.48**	
Total Number:	**3**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
Laws Calley	0.23
Philippe Staib	0.15
FTE Equivalent:	**0.38**
Total Number:	**2**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

The Auger Probe allowed, for the first time in an MBE environment, qualitative detection of the amount of material deposited on the surface by measuring the intensity of the Auger peaks. Testing, starting from pure elements to binary and ternary alloys, was performed and delivered a vast amount of data, showing dynamic changes of the sample surface.

Besides its value as an MBE growth monitoring tool, use of the Auger Probe to follow other processes should be investigated, like cleaning of the surface by heating (deoxidation process) or atomic diffusion.
During the Phase 1, in addition to the planned material growth, a variety of test studies were tried. Further investigations should expand these studies, using the Probe with a wider range of sophisticated materials and with other growth techniques, such as PLD.

Chemical Analyzer for *In Situ* and Real Time Surface Monitoring for Composition Control During Synthesis of Compound Semiconductor Films

Table of Contents

Foreword

The objective of the Phase 1 work was to test an innovative approach using a new design for an Auger Electron Spectrometer (the Auger Probe) that provides *in situ* and real time capability to monitor growth of compound semiconductor materials during MBE growth. As a result of the Phase 1 work, it has been shown that the Auger Probe is viable as an *in situ* real-time chemical monitoring tool for MBE. Collected information can be used to guide the growth process of materials for which the actual surface conditions are critical. The Auger Probe, after improvements and software updates for real time, continuous, multiple line acquisition, should prove to be a well suited tool for the characterization of *in situ* material growth. Additionally, no limitations were noted that would prevent the use of the Probe for materials beyond those tested or in other growth methods, like PLD.

Statement of Problem

The aim of our work throughout the Phase 1 project has been to demonstrate the feasibility of using the Auger Probe in an MBE environment for *in situ*, real time measurements of the atomic composition of a growing surface without impacting the MBE process. In past years, it has become evident, especially for some materials, that *in situ*, real time chemical information would be extremely helpful in a growth environment. Past attempts to this end have not provided a solution. Recently, surface analysis tools have been added in adjacent chambers so that materials can be examined without removal from vacuum, but this method does not allow for real-time monitoring. Utilizing a totally new approach to an energy spectrometer, the Auger Probe, coupled with an electron excitation source that is compatible with growth conditions (the existing RHEED source in this case), the Phase 1 project team has endeavored to test the viability of identifying the real-time chemical make-up of a growing surface.

Phase I Project Overview

Initially, in Objectives A, the Auger Probe system, hardware and software plus the RHEED system, were prepared for Phase 1 to work in a VEECO MBE chamber located at ARL. Software was upgraded to include the specific materials identified for this project. Probe electronics were calibrated. A clone system was installed in a demo chamber at SI for back-up testing. Project team members were trained to use the Probe system and to select the parameters of the Auger technique needed to operate in various growth scenarios.

As preliminary steps for the growth experiments, a series of pre-growth monitoring of simple operations was defined, Objectives B.1. First, the Probe was used to obtain spectra of relevant single elements, "reference samples", to help the team calibrate the spectra peaks and test the operation of the Probe with well-defined experiments. After successfully collecting this reference data, cleaning of GaSb substrates to be used in growth was monitored. The AP spectra indicated the desired removal of the oxygen. Similar results were obtained for InAs, allowing the cleaning process to now be done *in situ* rather than using a time consuming hydrogen cleaning method. Later, InAsSb growths on the InAs cleaned in this manner were successful, confirming the Probe results about oxygen removal. For each iteration of this process, reproducibility of the process was confirmed from the resulting spectra. The Probe was found to give reproducible Auger spectra without impacting the MBE process.

As defined in Objective B.2, the primary activities of the Phase 1 project were to monitor actual MBE growth. Multiple AlGaSb and InAsSb growths were monitored during the entire growth process. For each growth element, the Auger peak range was separately monitored. For example, using the direct Auger and the lock-in signals for AlGaSb, changes in the Ga and Al peak followed expected changes in composition, while the Sb peak shape and intensity remained nearly unchanged (within 1%). InAsSb was grown with spectra continuously collected. The results were analyzed for layer by layer insight into the growth process, providing evidence of changes in the atomic composition of the layers. (See Appendix B2.4B for the details of this investigation.) Additional experiments of interest to team members were performed to further test the use of Probe monitoring. GaN growth was monitored for information about the conditions when the growth changes from N rich to Ga rich. In summary, many and varied growths were successfully monitored by the AP, without equipment failure; however, further processing of the growth spectra requires a more refined model.

Abbreviations used: **ARL** = Army Research Lab, Adelphia, MD.
                                  SI = Staib Instruments Lab, Williamsburg, VA.
                                  SB = Stony Brook University, Stony Brook, NY.
                                  AP = Auger Probe.

For the Objective B.4, various data processing routines were employed to study the Auger spectra collected. Using one approach, LabView routines were developed to analyze the spectra. In another, MathCad routines were written to process the spectra through a series of filters. For Phase 1 results, these methods produced useful qualitative information, but further improvement is needed to optimize the strengths of the technique. A model must be developed and software implemented that is specific to dynamic Auger monitoring layer by layer real-time growth. Preprocessing by firmware may be needed for real time acquisition to input to growth decisions.

The Phase 1 project to test the feasibility of Auger monitoring during MBE growth both *in situ* and real-time has resulted in a wealth of run time data to analyze. The equipment performs dependably without impacting the MBE process. The Auger spectra reproducibly track expected growth events while adding insight to dynamic surface conditions previously not observable. The data processing developed by the team provides sufficient information for evaluations needed for Phase 1 feasibility studies.

Phase 1 Summary of Results

Project Goal - The aim of the Phase 1 project plan is to demonstrate the feasibility of using the Auger Probe in an MBE environment for *in situ*, real time measurements of the atomic composition of the surface without impacting the MBE process.
To meet this goal, Phase 1 included the following project objectives (see chart below for status).

A. Instrumentation Objectives were established to:

A.1. Modify the existing Auger Probe system for MBE application to ensure the most reliable and reproducible data is obtained.
A.2. Utilize a second, reference AP (not in a growth chamber) to calibrate the instrumentation and compare the results using reference samples.

B. *In situ,* real time data collection and processing objectives:

Data Collection *in situ* and in real time
B.1. Obtain reference spectra from selected reference materials, including substrates to be used in MBE, using both the *in situ* and the laboratory Probe. Obtain spectra during cleaning.
B.2. Collect AES data during multiple and selected MBE growths of Group III/V elements and evaluate data for any drift in accuracy over time.

Data Processing
B.3. Evaluate any impact from the instrumentation on the MBE process.
B.4. Evaluate and select the best algorithms for quantification of the data.

Phase 1 Tasks to meet Instrumentation Objectives A

Objective	Description:	Status
A.1.1	Prepare existing ARL Probe for use in the project.	Done
Comments:	Probe was refurbished, recalibrated, tested, and reinstalled in the MBE chamber at ARL.	
A.1.2	Develop electronic microprocessor control unit to control the excitation electron beam current intensity and stabilize the beam position and energy.	Ready for use with AP.
Comments:	Design and pretesting completed at SI. Finalize control unit, adjust for low energy.	
A.1.3	Upgrade AP software control for more precise adjustment of the operating parameters for added reproducibility during growth.	Done
Comments:	Updated AP software at ARL to newest version, including specific spectra parameters for project. Trained team on use of software and user defined VIs.	
A.1.4	Examine environmental factors which can impact the operation of the Probe during growth in the test MBE chamber and implement necessary corrections.	Improvements to hardware are planned.
Comments:	Designed and manufactured beam shield to extend through cryoshroud. Make coils to increase beam steering for steeper angles and better Auger signal. Possible later improvements for excitation source to improve the signal.	
A.2.1	Use reference AP at SI to calibrate the instrumentation and to compare with the growth spectra using reference samples.	Done.
Comments:	The inability to clean samples on the laboratory chamber resulted in less use of the reference Probe for validation. Once ternary growth was begun, this was ceased.	

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                                  SI = Staib Instruments Lab, Williamsburg, VA.
                                  SB = Stony Brook University, Stony Brook, NY.
                                  AP = Auger Probe.

Phase 1 Tasks to Meet Objectives B *In situ,* real time data collection of reference materials and cleaning.

Objective	Comment / Description:	Status
B.1.1A	Obtain substrate reference distributions.	Done.
Comments:	To begin using the Probe, reference spectra were obtained for growth elements. See Appendix B1.1A.	
B.1.1B	Utilize the AP to monitor native oxide removal from the surface of epi-ready commercial GaSb substrates (cleaning).	Done.
Comments:	As a standard step prior to growth, the substrate was thermally deoxidized. The AP successfully monitored the evolving surface and was able to track the de-oxidation process for GaSb, GaAs, and InAs. In the case of InAs, the AP enabled thermal deoxidation without damaging the substrate and did not interfere with the deoxidation process. Appendix B1.1B presents the results of GaSb and InAs thermal de-oxidation.	
B.2.1	For pure GaSb surface, dynamically record evolution of Auger lines corresponding to the reconstruction.	Done
Comments:	Using the AP, the GaSb pure surface was monitored at a range of temperatures, beginning after the removal of the native oxide & continuing until the start of growth. This was repeated for nearly all GaSb growths. In some cases, the pure surface was monitored in conjunction with RHEED acquisition. By varying the substrate temperature of GaSb, it is possible to observe a change in the reconstruction pattern of the GaSb surface using RHEED. An attempt was made to detect changes in the Sb Auger distribution that correspond to the changes in the reconstruction pattern. The Sb Auger distributions do not exhibit a change in shape or intensity with respect to surface reconstruction. This demonstrates that, while the RHEED indicates a structural surface change, the Sb surface concentration remains unchanged. Appendix B2.1 presents the Sb Auger signal versus time during one ramp through the RHEED reconstruction temperature.	
B.2.2	During growth of GaSb buffer, monitor repeated growths for reproducibility. Confirm against known stoichiometric ratio.	Done.
Comments:	The AP reproducibility is exhibited in Appendix B2.1. Throughout the monitoring process, the signal shows little deviation in peak height and no noticeable change in peak shape.	

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                        SB = Stony Brook University, Stony Brook, NY.
                        AP = Auger Probe.

Phase 1 Tasks to meet Objective B, Data acquisition and reduction from monitoring during MBE growth of several materials.
Evaluate impact of Probe on MBE growth.

Objective	Comment / Description:	Status
B.2.3	Binary Growth. Grow GaN. Observe at varying Ga fluxes. Grow GaSb with monitoring.	Done.
Comments:	While most binary growths monitored by the AP were homo-epitaxial buffers or in conjunction with ternary growths, GaN was also grown. Unlike other binaries grown, GaN requires an optimized flux ratio of Ga:N to grow high quality crystalline films. GaN was grown to determine if the AP could identify the Ga-rich/N-rich crossover point by monitoring a GaN growth with increasing Ga flux. Typically, identifying the optimal Ga flux requires several growths. Using the AP spectra, the crossover point was identified in one growth. Appendix B2.3 details this experiment.	
B.2.4	Monitor ternary growth and study resulting spectra. Compare to ex-situ XRD results.	Done.
Comments:	Several ternary growths were performed, AlGaSb, AlGaAs, InAsSb, and InGaSb. The data recorded real-time during the growths demonstrates the AP's ability to track changes in surface composition, as confirmed by comparison to *ex situ* XRD. Results mapped positively to known and predicted growth behavior. Appendixs B2.4A and B2.4B discuss the results of these growths.	
B.3.1	Evaluate impact of use of AP on the MBE growth process.	Done.
Comments:	The presence and use of the AP does not exhibit any noticeable negative influence on the growth environment or on growths. The ternary growths showed no unexpected deviation in targeted growth composition when compared to actual composition as determined *ex situ* by HRXRD.	
Comments:	To test the effects of the higher current RHEED beam on growth, two identical super lattice samples were grown, one with a -5uA RHEED beam impinging on the sample and one with no RHEED. HRXRD and PL were used to detect any variations due to the electron beam. None were found. See Appendix B3.1A.	
Comments:	Long term use of AP in a growth environment has been without equipment failure. To date, both the Probe and the e-gun have been in a working MBE chamber for over nine months.	

Abbreviations used: **ARL** = Army Research Lab, Adelphia, MD.
                       SI = Staib Instruments Lab, Williamsburg, VA.
                       SB = Stony Brook University, Stony Brook, NY.
                       AP = Auger Probe.

**Phase 1 – Tasks for development of the most suitable data analysis technique
to Meet Objective B for *In situ,* real-time data processing.**

Objective	Description:	Status
B.4.1	Evaluate several data processing methods to process the Auger spectra obtained during MBE growth experiments.	Evaluation completed.
Comments:	The major physical factors were calculated for all growth elements, see Appendix B4.1. The result is that none of the common quantitative Auger calculations are accurate enough to be simply applied to the present real-time application. A special new model must be developed to accurately describe the layer-by-layer growth process. Testing of algorithms and quantitative modeling was preformed using three different processing software packages: LabView, MathCad, and Origin. LabView seems best for real-time processing, MathCad offers very powerful and fast data processing, whereas Origin is a less powerful option (and has difficult licensing regulations).	
B.4.2	Test selected algorithms on both the integrated signal and the Auger distribution to assess the most accurate and the fastest procedure for recovering absolute Auger line intensities.	Testing completed.
Comments:	The test of algorithms was performed on the direct and the differentiated signal. Best results were obtained using the differentiated, lock-in signal. The Auger line intensities were measured as peak height, integrated peak, and using the derivative of the peak signal. All methods lead to a fair agreement with the expected values, with the limitations being due to the signal-to-noise ratio (for a few Auger lines only) and the lack of an accurate theoretical model. Data measured were dispatched to the different groups, processed separately using different software and then compared. See Appendix B4.2.	
B.4.3	Use the Auger line intensities to calculate the corresponding atomic concentration using models describing the Auger electron emission process and the escape depth of the electrons.	As far as possible.
Comments:	The common data processing for quantitative Auger spectroscopy was used and was able to deliver a fair description of the expected data; however, the lack of a theoretical model became obvious. The quantitative result was not so much limited by the accuracy of the Auger Probe as by the lack of knowledge of the correction factors in the calculation of the atomic densities.	

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                                  SI = Staib Instruments Lab, Williamsburg, VA.
                                  SB = Stony Brook University, Stony Brook, NY.
                                  AP = Auger Probe.

Conclusions

As a result of the Phase 1 investigations and experiences, the following conclusions can be made with respect to the results of this project.

Instrumentation

The new Auger Probe, designed and built by Staib Instruments, performs very well and is able to analyze the surface composition during growth without disturbance to MBE. The reproducibility of the spectra is very good, 1% or better for major Auger lines. The probe shows no aging, reliability, or stability problems in spite of nine months in a growth chamber and the heavy amount of materials to which it has been exposed. The acquisition time is compatible with the process speed of growth.

Changes to the excitation beam source can be implemented to increase the signal. Computer control of the beam parameters should be added.
The acquisition of weaker Auger lines is not yet satisfactory and should be improved by optimizing the beam angle and acquisition parameters.
The additional capability of the Auger Probe to operate in Energy Loss Spectroscopy was briefly tested at ARL and provided very valuable data which are complementary to the Auger data. Further testing of ELS could be rewarding.

Value as a growth monitor tool (Testing at ARL)

The Auger Probe allowed, for the first time in an MBE environment, qualitative detection of the amount of material deposited on the surface by measuring the intensity of the Auger peaks. Testing, starting from pure elements to binary and ternary alloys, was performed and delivered a vast amount of data, showing dynamic changes of the sample surface.

Besides its value as an MBE growth monitoring tool, use of the Auger Probe to follow other processes should be investigated, like cleaning of the surface by heating (deoxidation process) or atomic diffusion.
During the Phase 1, in addition to the planned material growth, a variety of test studies were tried. Further investigations should expand these studies, using the Probe with a wider range of sophisticated materials and with other growth techniques, such as PLD.

Impact on MBE growth (Testing at Stony Brook University)

The AP uses an electron beam to generate Auger emission, giving concern about the influence of the beam impact on the quality of the grown material. After a multiple layer growth under electron impact, the crystal quality was tested by X-ray diffraction and photoluminescense. There is no noticeable modification to the grown structure under electron irradiation.

Data processing (Performed at ARL, Staib Instruments, and Stony Brook University)

Data processing allows the measured intensity of the Auger lines to be converted into quantitative atomic densities. A number of classical processing models were used and different approaches were compared, using different programs such as LabView (at ARL), MathCad (at SI), and Origin (at SBU). Results always reflected the trend expected from the growth conditions.
The accuracy of the results appears to be highly dependent on the number of physical parameters included in the modeling. Phase I results clearly show that better Auger modeling is required in order to quantify the measurements, especially in real time. Preprocessing of the spectra using firmware is an option to explore for added processing speed. A model tailored specifically for layer-by-layer growth should be developed and implemented, with the capability to communicate measured results to other functions of the growth environment.

Abbreviations used: **ARL** = Army Research Lab, Adelphia, MD.
                      SI = Staib Instruments Lab, Williamsburg, VA.
                      SB = Stony Brook University, Stony Brook, NY.
                      AP = Auger Probe.
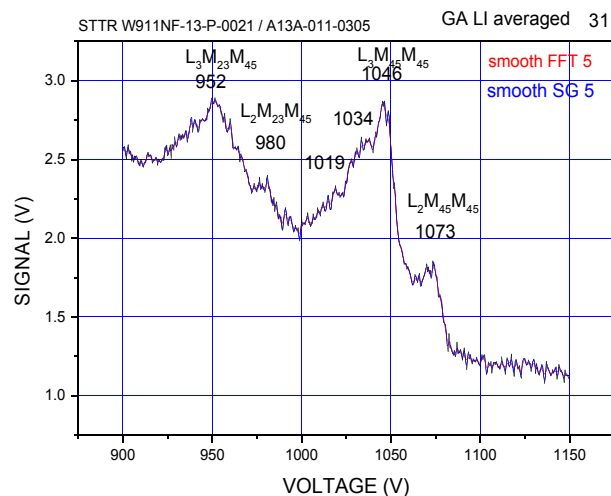
Task: Obtain reference spectra of elemental growth from ARL MBE system and calibrate AP. Some excerpted examples:
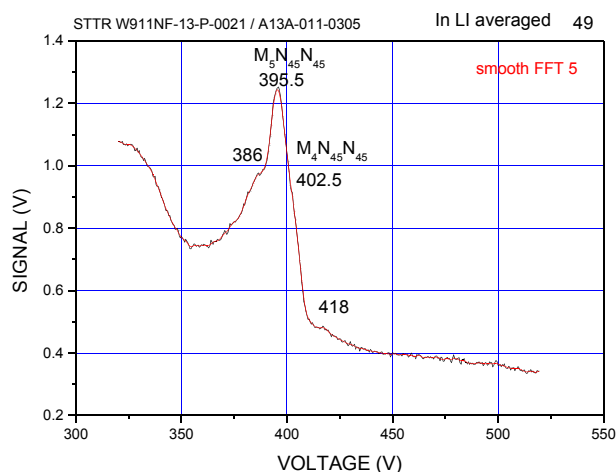
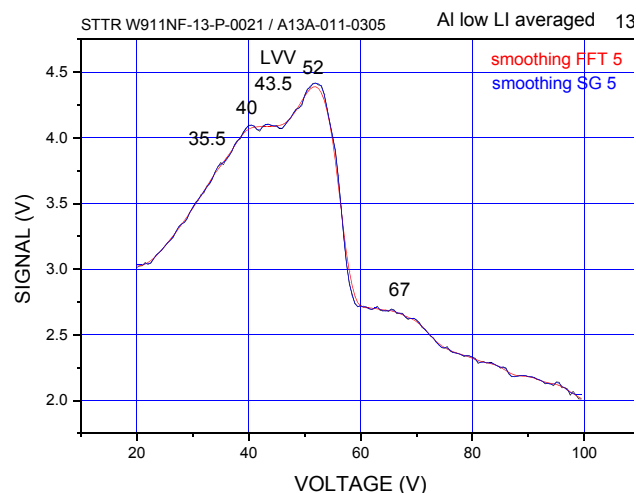## Indium   ## Gallium
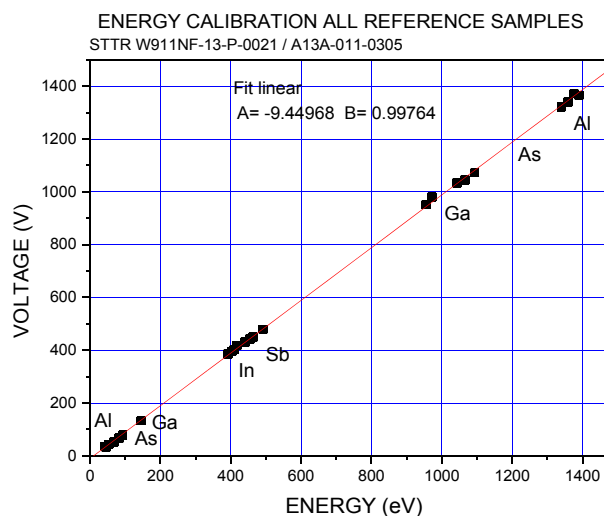

## Aluminum   ## Energy Calibration

The analyzer voltage is calibrated using tabulated values for the different Auger lines. A linear calibration curve can be used to convert voltage from the Probe to energy of the lines.

Deoxidation Monitoring for GaSb and InAs Substrates

A contamination free growth surface is critical to the growth of high quality crystalline films. In the growth of III-V material systems, one of the primary growth surface contaminates is oxygen. Typically, an in-vacuum deoxidation step is required prior to growth on the substrate. The AP was used to monitor the deoxidation of the growth substrates GaSb and InAs. Most growths performed for the STTR were grown on GaSb, so thermal deoxidation of these substrates was monitored several times by the AP.
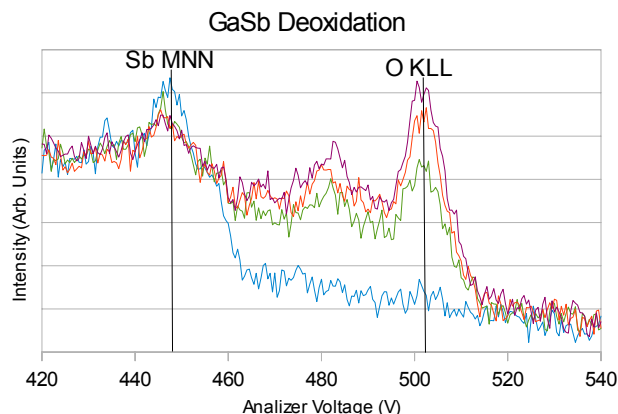
Figure 1 shows the typical deoxidation recorded in preparing the GaSb wafer surface for growth.

The substrate was ramped to 550 °C under an Sb overpressure. As the substrate temperature was increased to 610 °C, a rapid decrease in the oxygen signal is noted. Once the oxide is removed, a strong Sb signal is recorded. Since the AP tracked the evolution of the surface during the thermal deoxidation of the GaSb wafer, a more challenging deoxidation study was attempted.

Thermal desorption of oxygen from the InAs surface typically results in the decomposition of crystal surface. Furthermore, RHEED monitoring of surface deoxidation lacks the sensitivity to ensure complete deoxidation of the growth surface. Typically hydrogen cleaning of the surface is employed to remove the native oxide. The process is time consuming, requiring extended pumping times to evacuate the hydrogen. Atomic hydrogen is required for the cleaning process, necessitating special equipment, including a hydrogen cracker, to clean the wafer.

In the experiment, an InAs wafer was heated to near the deoxidation point in the MBE chamber, under an As overpressure while monitored by the AP. To ensure that the deoxidation temperature was not exceeded, the substrate was then ramped at 0.5 degrees/min in 10 °C increments until the oxygen Auger signal began to decrease. The decrease in signal was noted at 510 ° C. The substrate was held at 510 °C. After about 16 minutes no oxygen signal was detected.

To confirm adequate oxide removal, the InAs surface was subsequently used for growth. The growth resulted in an epitaxial film, consistent with film qualities of those grown on an InAs surface prepared by hydrogen cleaning.

In situ monitoring of the deoxidation process ensures a clean, high quality growth surface. In the case of InAs, *in situ* monitoring enabled the used of thermal deoxidation rather than the more commonly used hydrogen cleaning process, saving time and eliminating the need for a hydrogen cracker source. While the presence of the AP ensured clean samples for the growths, it in no way interfered with the deoxidation process.

Sb Signal Monitored during Surface Reconstruction Change

The Sb Auger line of homo-epitaxial GaSb was monitored for variation during several temperature ramps through its reconstruction temperature. The surface reconstruction was observed simultaneously by RHEED. Figure 1 is a 3D plot of the Sb Auger line versus time. The Auger line shows no change in Sb surface concentration. This indicates that while the structure of the surface is changing, based on RHEED observations, the Sb surface concentration is not changing.
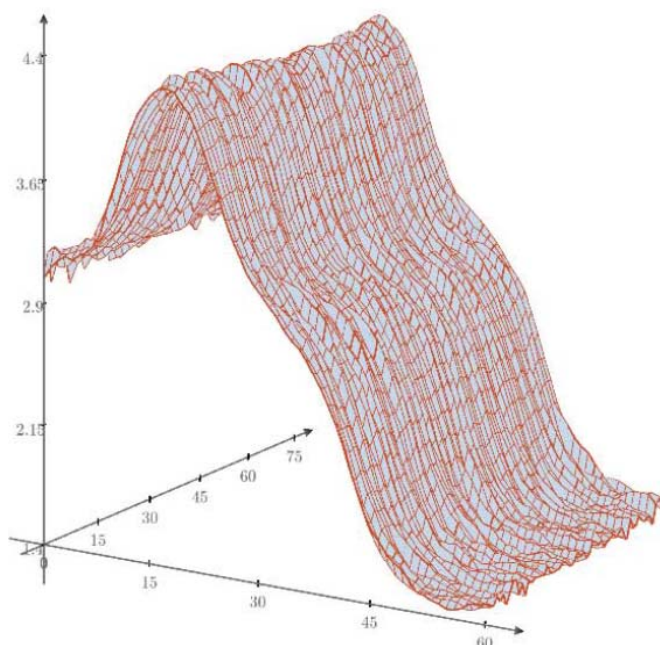
Figure 1. Sb Auger spectra versus time

It should also be noted that the shape and peak height of the Sb line are not changing or varying with time, indicating very reproducible results with the AP.

Determination of N- and Ga-Rich Growth Conditions for GaN, Using in-situ Auger Electron Spectroscopy

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Army Research Laboratory
2800 Powder Mill Rd, Adelphi, MD 20783

Summary Abstract

An in-situ electron probe was used to detect Auger electrons from Ga and N, which allowed the determination of the surface chemical composition during MBE deposition of GaN. The instrument was used to identify the important 1:1 flux boundary between Ga- and N-rich deposition conditions.

———————————————————

ARL is collaborating with Univ. of Nottingham and Berkeley National Labs to develop electrodes for water splitting, using highly-mismatched alloys (HMAs) of GaN mixed with dilute concentrations of As or Sb.

In contrast to conventional III-V MBE-growth, which is performed under group-V rich conditions, state-of-the-art GaN is grown under slightly Ga-rich conditions at very high substrate temperatures (~800 C). With this background in mind, our colleagues at Univ. of Nottingham started growing GaNSb under Ga-rich conditions, at very low growth temperatures in order to avoid phase segregation. Surprisingly, we found that it was not possible to change the bandgap with increasing Sb-concentration following this approach[i]. Instead the bandgap appeared to be dominated by a defect state. However, by switching to N-rich conditions, the bandgap was observed to change and roughly followed the predictions of the band-anti-crossing model[ii].

These examples illustrate that determining the critical Ga-flux where the growth changes from N- to Ga-rich is very important. The flux ratios from other III-V elements can be measured by an in-situ beam flux monitor and the fluxes for stoichometric growth can be determined using RHEED oscillations on a single sample. However, in the case of the beam from a nitrogen source, the active N-content is usually not known and RHEED oscillations are not observed. For conventional GaN growth the typical procedure for determining the critical Ga-flux is therefore to fix the N-flow while increasing the Ga-flux. Under these conditions it may be possible to observe a change in the RHEED pattern on a single sample, but more typically a series of films are produced and the growth rate determined. Ga-rich conditions are established when the growth rate as a function of Ga-flux ceases to increase. For HMA growth this would be the only method available since the RHEED pattern does not exhibit a clear transition.

The growth of such a series is very time and resource consuming, especially if it needs to be done at different temperatures. Typical substrates for GaN are extremely expensive. Here we will demonstrate a new, very fast, method enabled by the use of the Staib electron probe that allows measurements of Auger electrons excited by the RHEED gun.

In these experiments, Si (001) and Sapphire (0006) substrates were outgassed at 800 C and then ramped to 325 C before deposition (measured by thermo-couple). A Veeco Uni-bulb N-plasma source was used at a power level of 400 W and the N_2 flow rates were varied from 0.22 to 0.58 sccm. The pumping was done with a CTI-8 cryo-pump and standard cryo-paneling in a Gen II MBE system, resulting in a steady-state background chamber pressure of 1.5×10^{-5} Torr at the highest flow rate. The Ga source was set up to generate a linear flux ramp from 9.81×10^{16} to 3.92×10^{18} at/m^2/s over two hours. During this ramp the Auger signals for N (375 eV), and Ga (1050 eV) were repeatedly recorded.
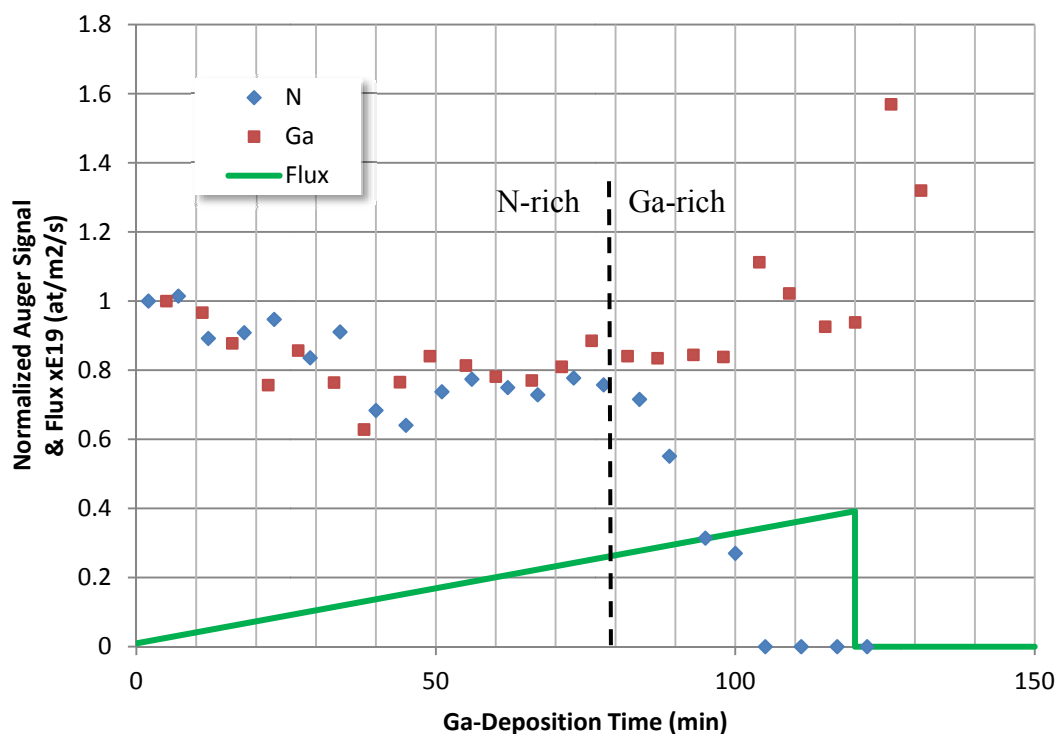
Fig 1. The normalized Auger signals from N and Ga as a function of Ga-deposition time. The Ga-flux is shown as a green line. The N-flow was 0.58 sccm.

As expected, both the Ga and N signals increased as a GaN film was starting to form under N-rich conditions (grown separately and not shown here). Shortly after the start of the continued GaN growth, both the Ga and N signals started to decline and reached a steady state at around 50 minutes as shown in Fig. 1. It is unclear why this decrease in signal strength happened. Since we assume that stoichiometric material is being grown, we can speculate that it is a surface roughening effect.

After 80 minutes the N-signal showed an abrupt decline, while the Ga stayed constant. We assume that the 80 min point is where the Ga and N-fluxes are equal. The Ga-flux at this point was 2.5×10^{18} at/m^2/s, which corresponds to a growth rate of 0.27 micron/hr on GaSb. (The growth rate on Sapphire must be determined separately since it depends on the crystalline structure of the GaN).

Once a continuous layer of Ga was formed at around 105 min, no more N could be seen and the Ga signal increased abruptly. It is unclear if the following apparent decline in the Ga-signal is real.

At 120 min the Ga and N shutters were closed. Another very significant increase in the Ga-signal was then observed. We can speculate that this must be another surface structure effect that will require further studies.

We are not showing the corresponding experiments from the Si substrates. Qualitatively similar results were observed but the critical Ga-flux was noticeably lower. We do not understand this difference, which implies that the N to Ga-rich transition is substrate dependent. It could be caused by a difference in real substrate temperature, the crystalline structure or both. GaN is polymorphic, and it is unknown what the crystal structure is at this low growth temperature on Si. Past experiments indicate that GaN on sapphire grown with these conditions is polycrystalline, with a tendency to align along the (0002) growth plane. More studies would need to be done in order to clarify this difference in the critical Ga-flux for the N rich to Ga rich transition.

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[i] GaN1-xSbx Highly Mismatched Alloys Grown by Low Temperature Molecular Beam Epitaxy under Ga Rich Conditions, WL Sarney, SP Svensson, SV Novikov, W. Walukiewicz, CT Foxon, Journal of Crystal Growth, 383, 95-99 (Nov 15 2013).

[ii] K. M. Yu, W. L. Sarney, S. V. Novikov, D. Detert, R. Zhao, J. D. Denlinger, S. P. Svensson,2 O. D. Dubon,1,2 W. Walukiewicz,1 and C. T. Foxon, "Highly mismatched N-rich GaNSb films grown by low temperature molecular beam epitaxy", Appl Phys Lett 102, 102104 (2013).

Summary of results of Ternary (AlGaSb) growth sequence monitored in-situ real-time using Auger Probe - data processing using MathCAD.

Process High Energy Sequence AlGaSb
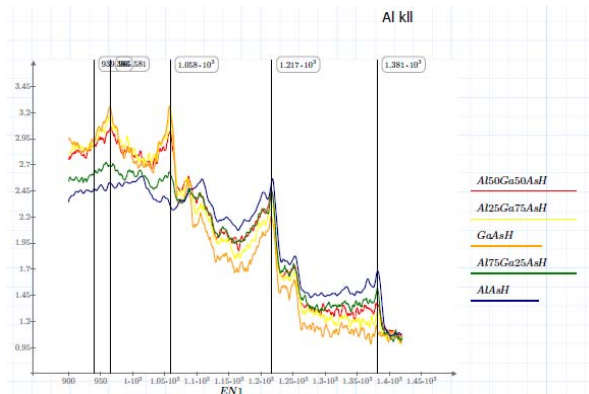
Extract Profiles
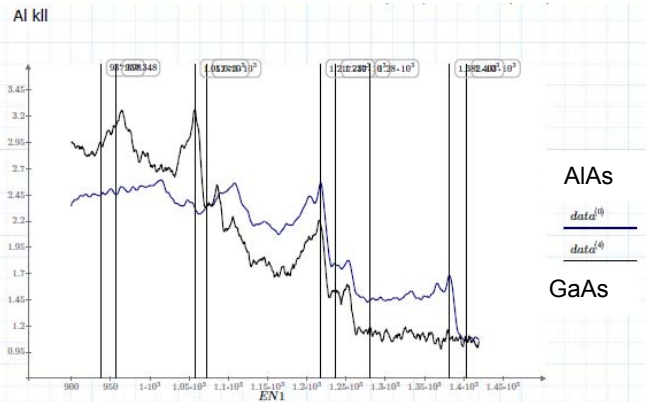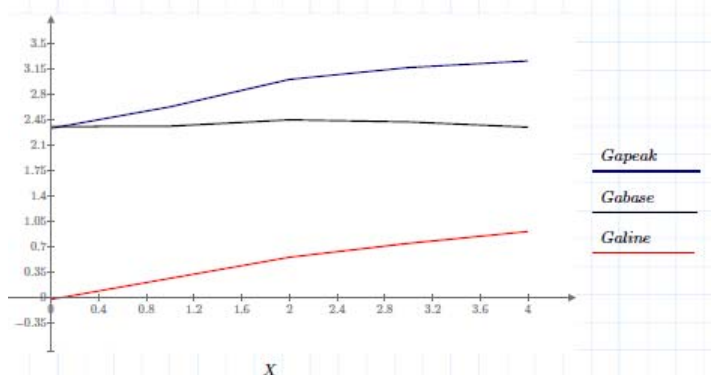

Plot of AlAs and GaAs

Al Profile
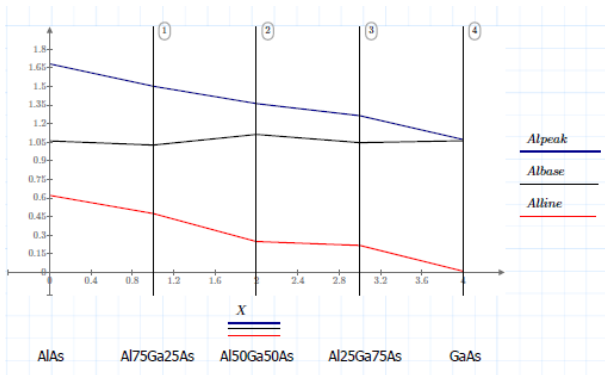
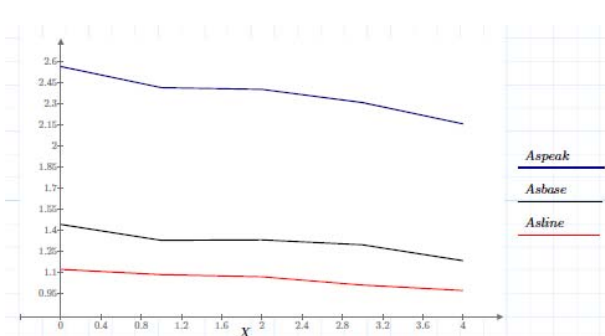Alline = Alpeak – Albase
Al kll peak and base energies-1382, 1403eV

Ga Profile

Galine = Gapeak – Gabase
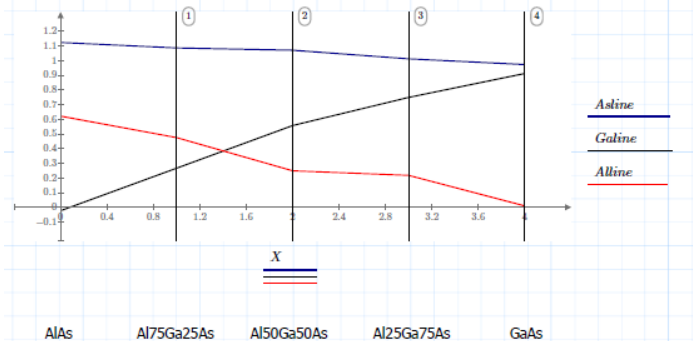Ga lmm peak and base energies-1057, 1073eV

As Profile

As line = Aspeak – Asbase
As lmm peak and base energies-1218, 1280eV

Plot of all Profiles of High Energy Auger Lines

A Preliminary Detailed Auger Analysis of MBE Growth Dynamics in InAsSb
Stefan P. Svensson and Wendy L. Sarney
Army Research Laboratory

Introduction

We collected spectra continuously during the growth of 5 layers of InAsSb with different mole fractions (sample K1495). After the growth the sample was left alone for a while and then exposed to a low level As flux.

The spectra were analyzed using two new Labview routines. In one method we selected a reference peak from an element and plotted the signal values from a test spectrum against the reference signal data. We then fit a straight line and identified the slope as the scaling factor. In the other method we used filtering and differentiation and defined the peak to peak value as the signal. This method requires further optimization but gave useful qualitative information in the low-energy range where the secondary electron background dominates.

The attached Excel file contains the numeric analysis. It opens with a very low magnification to show the contents. At the top is a list of the growth events and times. Below are the spectra in three rows; each one representing low, mid and high energy. In each graph the time starts from the bottom and time progresses to the right.

Under the spectra are graphs summarizing the numeric values extracted from the raw data, which is summarized at the bottom of the page.

The following is a description of our preliminary interpretation from each layer.
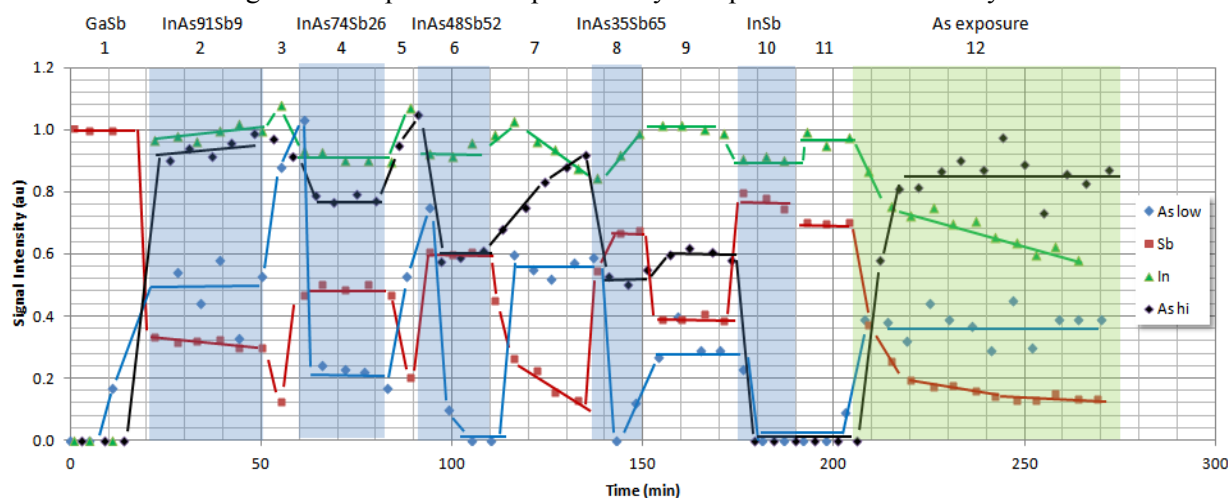
1. GaSb

A GaSb buffer layer was grown on a GaSb substrate. The As valve was closed during this deposition.

Apart from a small low-energy As signal, which is probably spurious, there were no In or As peaks visible as expected. The high-energy Ga peak can be seen in the high-energy As spectrum. The Sb mid energy peak was clearly visible, with an intensity that was substantially higher than exhibited for any other layer in the structure (even stronger than in InSb – see layer 10). A very low energy feature that appears to be Sb related was seen at ~25 eV. This is all consistent with pure GaSb.

2. LM InAs$_{0.91}$Sb$_{0.09}$

In order to avoid an unwanted conversion of the surface due to As leakage, the sample was turned 180 deg away from the sources. After the As and Sb valves were set to predetermined values, the sample was turned back to the growth position and the In, As and Sb shutters were opened simultaneously.

The Sb dropped rapidly, but **not** to a tenth of the intensity seen in GaSb. This is contrary to what one would expect based on the target mole fraction, and implies that the As/Sb mixture was not uniform on the surface. One could speculate that the stronger In-As bond compared to In-Sb pulls more As deeper into the group V surface mixture.

The high-energy As signal is at ~0.92 of its maximum value. This is close to the targeted value, and could mean that the deeper penetration allows it to properly sample the bulk composition.

The low-energy As signal is about half of its highest value. This is another indication that the As atoms are physically beneath the Sb atoms, otherwise the low energy As signal should also be at ~90% of its max value.

As the film grows, both the In and the high-energy As show an increasing intensity, while Sb drops. These trends look statistically significant and would imply non-uniform composition throughout the thickness of the layer.

3. Static layer after InAs$_{0.91}$Sb$_{0.09}$

All shutters were closed. The Sb valve setting was increased and the As valve setting was reduced and given ~ 10 min to stabilize.

The surface sensitive low energy As signal went up dramatically to its max value, while the Sb signal dropped to half of the intensity that it had in the bulk layer. The In signal increased slightly, which was seen in all static layers except the last one (11). The high energy As signal appeared to decrease by a small amount, but it is unclear if it was statistically significant.

The increase of the In could be interpreted as evidence of a stoichiometric surface that was no longer covered with excess group V elements (the growth was group V rich). Ample As was still available from the source, and exchanged with surface Sb. The high energy As signal appeared to be dominated by the bulk and showed little change.

4. InAs$_{0.74}$Sb$_{0.26}$

All the shutters were opened and closed simultaneously. The low energy As dropped down to about half the value exhibited in the LM InAs$_{0.91}$Sb$_{0.09}$ layer, or ~20% of its max value. The Sb increased to about 50% of the value in GaSb. The surface ratio was again more Sb-rich than the bulk composition, implying a non-uniform group V surface layer. The high energy As peak was about 0.76 of max, which is in reasonable agreement with the bulk value, again showing that it is mainly probing the bulk.

5. Static layer after InAs$_{0.74}$Sb$_{0.26}$

The Sb valve was kept the same and As valve reduced. The wait time was ~ 10 min. The behavior was similar to the previous static layer, except this time the high-energy As signal also increased, as opposed to being more or less static. In this case, the surface As/Sb exchange affected a larger fraction of the crystal, which means that a larger impact could be expected in the bulk dominated As signal. The waiting time was relatively short and did not obviously reveal sub-surface exchange like in 7 (see further down).

6. InAs$_{0.48}$Sb$_{0.52}$

The growth was started by opening all shutters simultaneously. The In signal returned to a similar value to what was seen in all growing layers. The bulk As signal decreased to ~0.6, which happens to be similar to the Sb signal. Although the As and Sb signals were similar, they were both higher than the mole fraction. The low energy As peak demonstrated an interesting behavior in that it seemed to drop and disappear over more than 10 minutes after the growth started. This indicates a time dependent redistribution from a more or less random As/Sb mixture to a layered one with Sb on top.

7. Static layer after InAs$_{0.48}$Sb$_{0.52}$

This was the longest static period. The Sb and As valves were kept at the same values as during the growth and the As valve was changed shortly before the growth of the next layer.

Just after the termination of the growth, the In signal initially increased, as it had after the prior layers. However, this time the In signal began to decrease after 10 min. The low energy As peak increased rapidly to an approximately constant level within the same time frame that the Sb signal decreased. This can be interpreted as the exchange of the top layer Sb with As. After this, a much slower decrease was seen in the Sb signal while the high-energy, bulk-dominated As signal increased in a pronounced way. We interpret this as evidence for an As/Sb exchange in the layers below the surface. It is unclear why the In drops. It is most likely due to As coverage. As the films become more mismatched and the surface exchange reaction progresses, the film becomes rougher, which can also affect the signals. However, in layers 8 and 9, the In signal recovered so roughening is a less likely explanation.

8. InAs$_{0.35}$Sb$_{0.65}$

As just mentioned, the In signal recovered during the growth of this layer to a value near its max. The Sb signal increased to 0.65 and the bulk As decreased to 0.52. The surface As was buried in the middle of the

Page 2

growth but started reappearing shortly before the end, although the signal was weak. Overall the interpretation is the same as in previous bulk layers.

9. Static layer after InAs$_{0.35}$Sb$_{0.65}$

This is also a relatively long waiting period. The As valve was closed early in order to reduce the As background pressure to a level sufficient for the growth of As-free InSb.

The development of the peaks differed from the previous long wait. In this case, the In signal remained constant at near 1. Both the low- and high-energy As peaks increased rapidly, but then saturated quickly at levels that were lower than in the previous case. The Sb peak dropped and saturated quickly, and then remained at a constant level.

It appears that the initial As/Sb exchanges happened rapidly in the first top layer, but the subsequent change that we earlier interpreted as sub-surface exchange did not occur here. The difference between the cases were the Sb mole fraction, which was higher in this layer, and the much lower As flux. It is not obvious why a material with less As would inhibit surface As from penetrating and exchanging for sub-surface Sb – the opposite would seem more likely. However, a lower supply of As would certainly slow down the exchange, so it looks like in this case the process is simply limited by the As supply.

10. InSb

The In and Sb shutters were opened simultaneously. The In signal exhibited a slight decrease and the Sb signal a rapid increase. A weak decrease in the Sb signal was seen during the deposition, but may not be statistically significant. Both the high- and low-energy As signals disappeared.

This behavior was consistent with growth of uniform InSb. There was no supply of As and the top surface layer of As was buried quickly. The drop in the In signal must be due to the Sb-rich growth conditions, and are confirmed by the recovery of the In signal and decrease of the Sb as seen during the subsequent waiting period.

11. Static layer after InSb

As already mentioned, the In signal recovered and the Sb signal dropped to a bulk representative value. Although the In signal remained roughly the same in all InAsSb layers, the Sb signal was noticably lower than observed in layer 1 (GaSb) or about 0.75. It is possible that this was partially a density effect due to the larger size of the In atom compared to Ga. The lattice constants of GaSb and InSb are 6.096 A and 6.479 A, respectively. In a given area or volume there would then be $(6.096/6.479)^2 = 0.89$ or $(6.096/6.479)^3 = 0.83$ less Sb in InSb than GaSb. The choice of square or cube would depend on the probing depth. (We need more literature searching to understand this effect better).

12. As exposure

The As valve was opened to 150 mil while the As shutter remained closed.

This resulted in a rapid drop of the Sb signal followed by a slower decline. The low energy As peak increased rapidly and then remained constant. A similar trend was observed for the high-energy As peak. The In signal dropped quickly for about 10 min and then declined at a much slower rate.

It appears again that the Sb in the top layer was quickly exchanged with As. Based on the behavior during previous waiting periods – particularly 7 – we would expect a sub-surface exchange to proceed after this. All signals except the high-energy As were consistent with this. However, the noise is very pronounced for this As data set. The quality of the surface in general was poor as could be seen by strong light scatter. It appears that the high-energy spectrum was particularly sensitive to this.

Conclusions

The growth of InAsSb appears to proceed in a complex and non-intuitive way. The very top surface during growth is not homogeneous and its composition is not representative of the bulk layer underneath. In order to use the probe for composition control we need to understand the relationship between the surface layer and the bulk under various flux ratios and temperatures. Alternatively, we could study only the high-energy peaks since they seem much more representative of the bulk. Unfortunately the high-energy Sb-peaks are above the range of the probe. Also the signal to noise ratio in the high-energy range would need to be significantly improved.

Either way, we think this is an outline for a very exciting phase II project.

One possible effect of using the Probe to monitor a growing film is the interaction between the growth layer and the RHEED beam that is used to generate the Auger electrons. While RHEED is often used to monitor a growing film, it is typically used at a low beam current and/or not left to impinge on the sample for extended periods of time.

To ensure that the RHEED beam did not have an impact on the growing film, two samples were grown. The first was grown using standard growth conditions. The second sample was grown with the same growth conditions, but with constant irradiation by a -5 µA electron beam. The samples contained four triple-layer quantum wells and were designed to have photoluminescence (PL) spectra near 4 µm at room temperature. The HRXRD omega/2theta scan preformed on each sample after growth exhibited no structural deviations between the two films, Figure 1. The PL spectra indicates that the luminescent properties were also unaffected by electron irradiation, Figure 2.

One can conclude that the electron beam excitation required for reliable and efficient operation of the Auger Probe does not interfere with the MBE process and does not affect structural/optical quality of the antimonide-based photonic heterostructures.
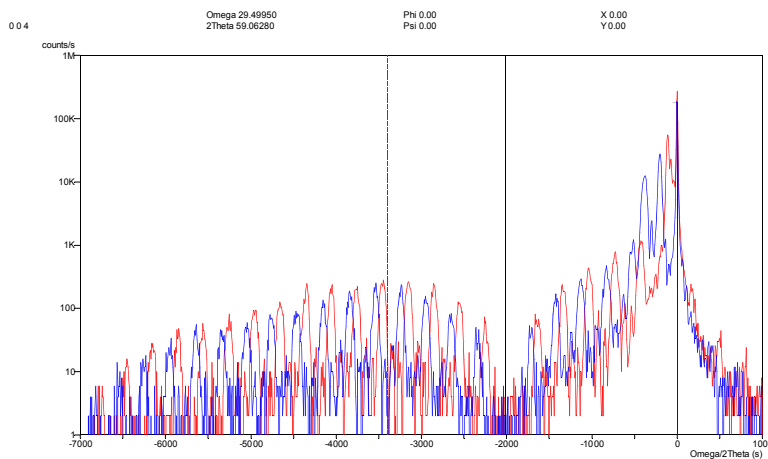
Figure 1. HRXRD of super lattice structure. Blue without RHEED. Red with RHEED.
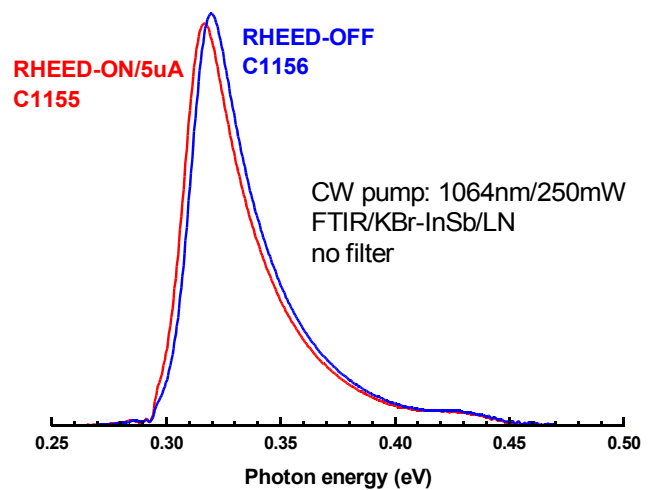
Figure 2. PL of super lattice structure. Blue without RHEED. Red with RHEED.
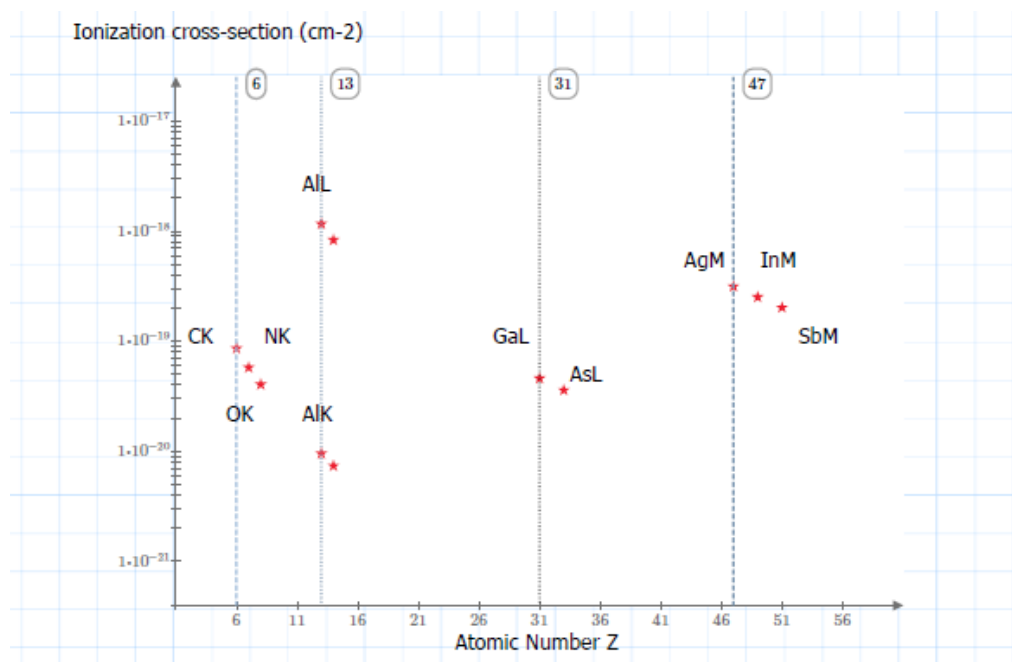
Figure 1 Plot of the Ionization Cross Sections at 12keV Beam Energy
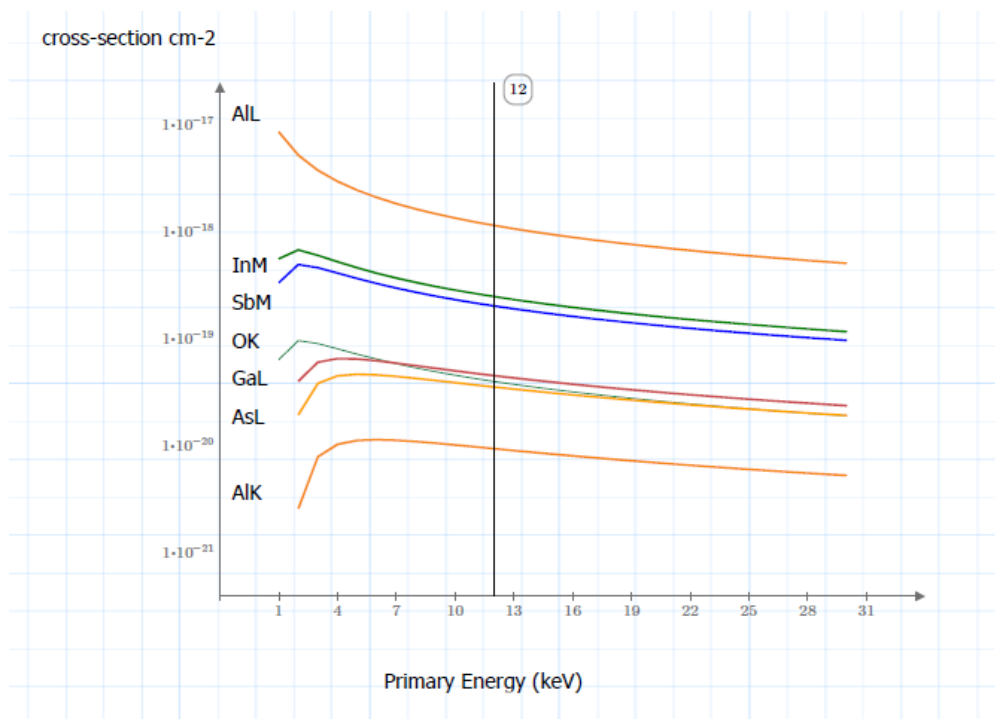
Figure 2 Plot of the Ionization Cross Sections versus Primary Beam Energy

Prepare algorithms to assess the most accurate and the fastest procedure for recovering absolute Auger line intensities.

Algorithm Evaluation Process Overview - One Method Evaluated

1. **Import a sequence of spectra with indexing. Plot, pack, and save data matrix.**
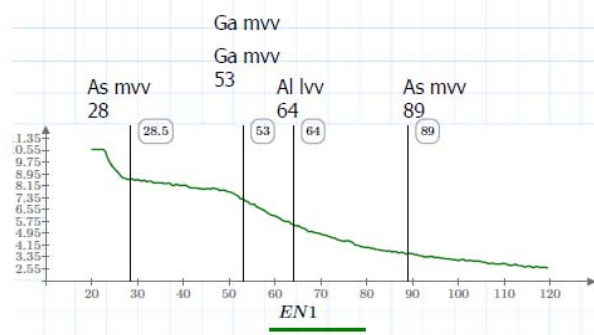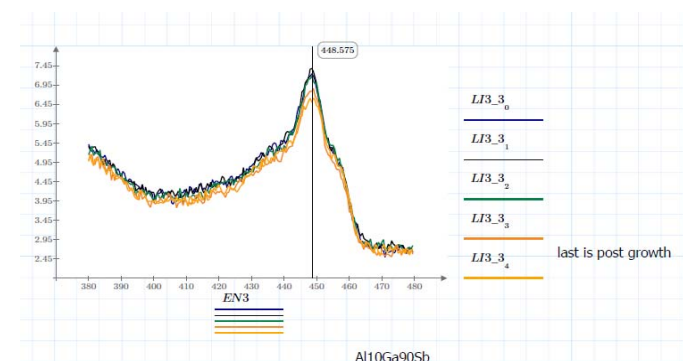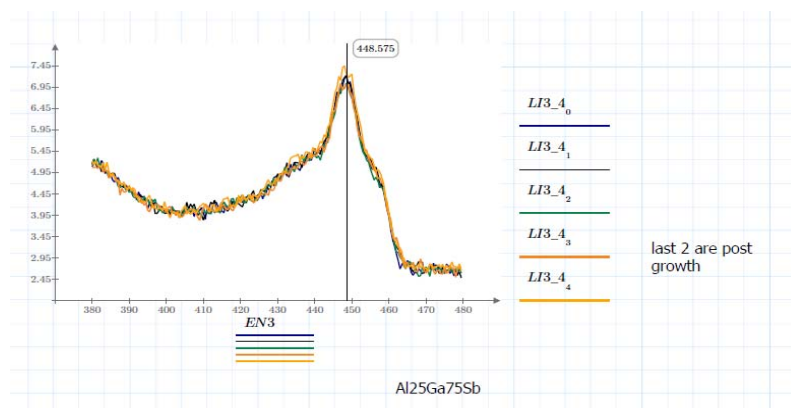

Import GaSb low energy range
1 single scan
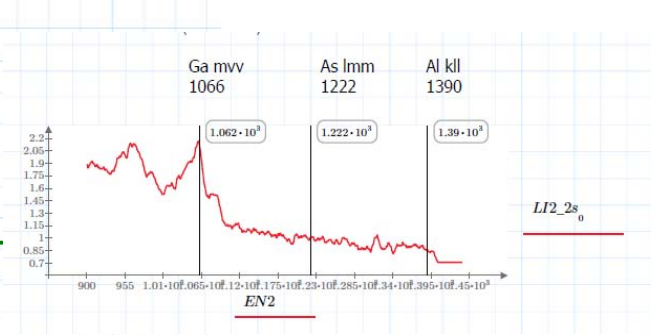
Import GaSb high energy range
2 single scans
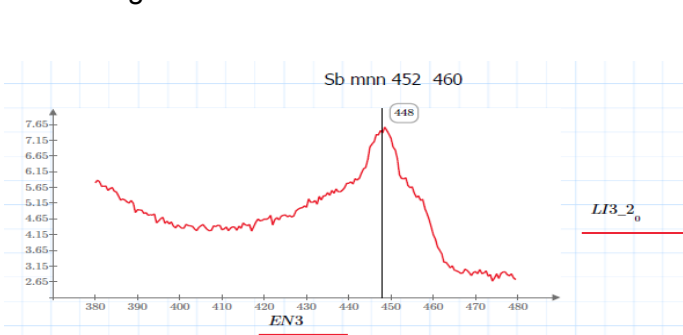
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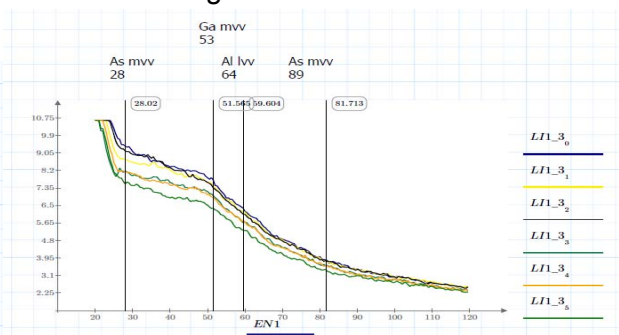
Import AL10Ga90Sb low energy range

Import AL10Ga90Sb mid energy range
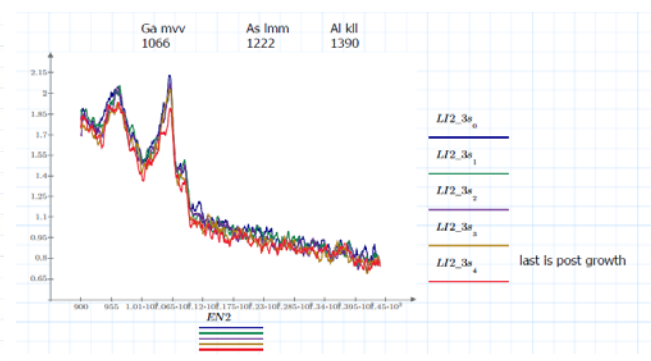
Import AL10Ga90Sb high energy range

Prepare algorithms to assess the most accurate and the fastest procedure for recovering absolute Auger line intensities.
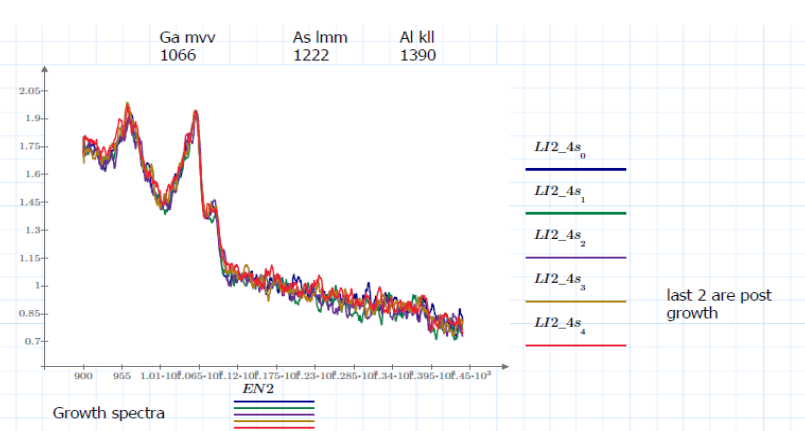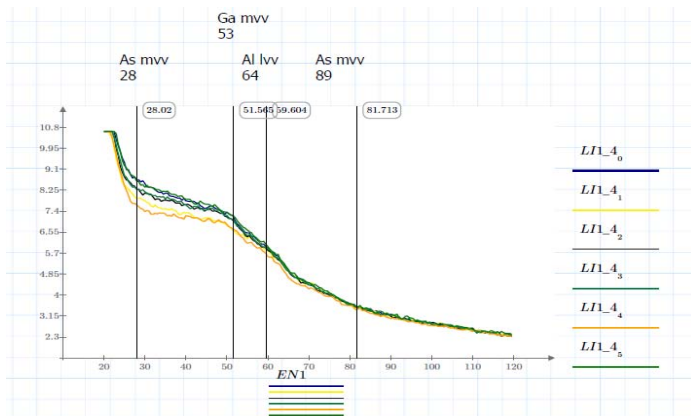
Import AL25Ga75Sb low energy range

Import AL25Ga75Sb high energy range

Import AL25Ga75Sb mid energy range

Continue for all growth spectra.   Build matrix and save matrix.

3. Data Processing – Ga Al As Ternary – nopeak fitting, manual peek selection
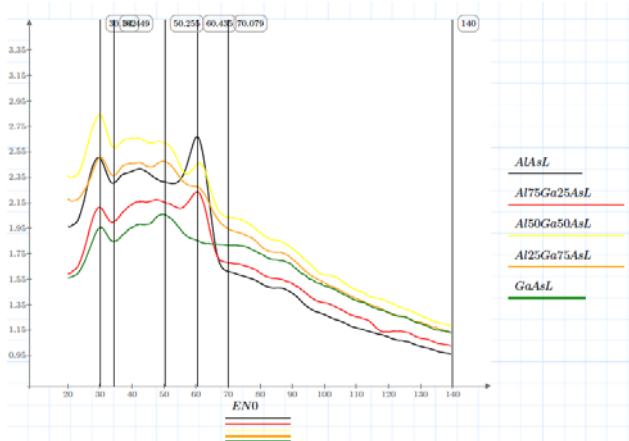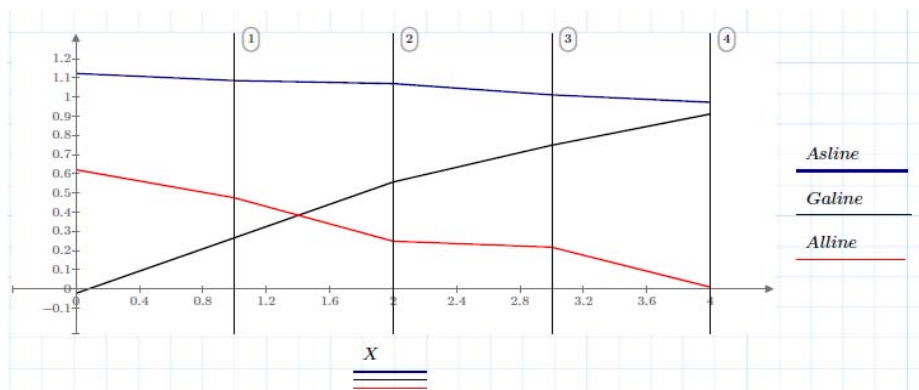

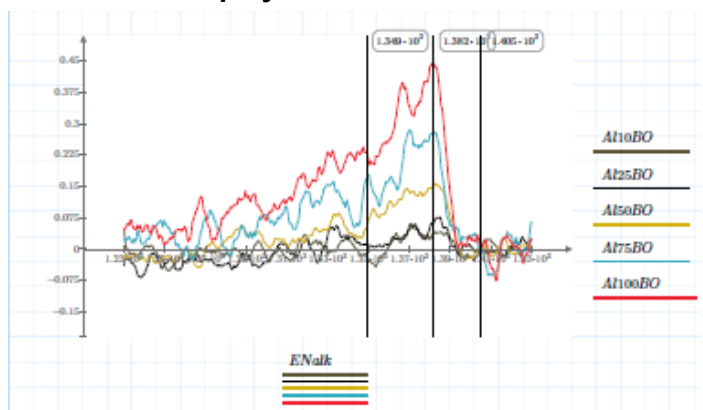Plot of the low energy range AlGaAs sequence
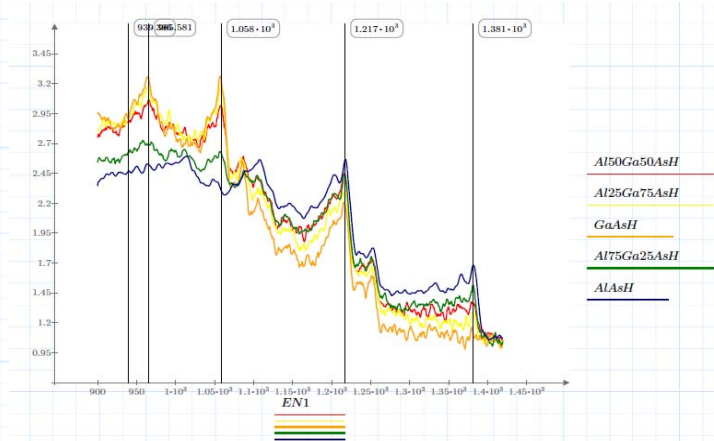
Process High Energy Sequence AlGaAs-

Prepare algorithms to assess the most accurate and the fastest procedure for recovering absolute Auger line intensities.
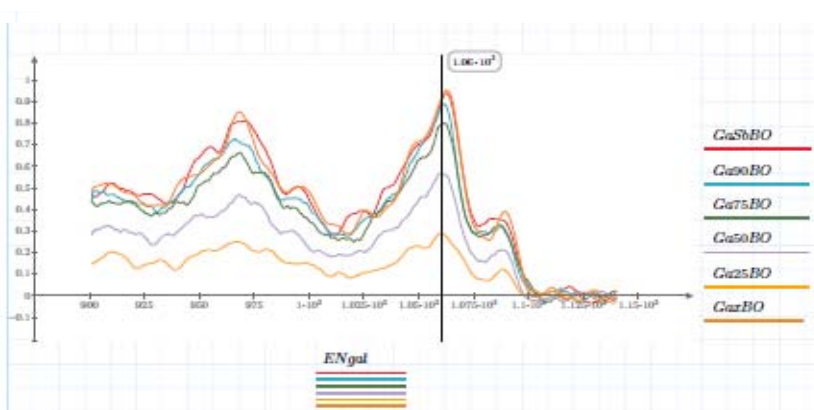

Build a matrix - Plot all Profiles of High Energy Auger Lines

4. Display Growth Profiles

Subtract background and energy offset

Select Ga Imm energy window-
Range 900-1140eV-
Plot and smooth data-
Subtract background and offset -

A. Abstract Submitted for Conference April, 2014

Development of AlInAsSb for M-LWIR Detectors, Using In-Situ Auger Electron Spectroscopy

Stefan P. Svensson[1] Wendy L. Sarney[1], Harry S. Hier[1], Ding Wang[2], Dimitry Donetsky[2], Gela Kipshidze[2], Leon Shterengas[2], Youxi Lin[2], Gregory Belenky[2], and W. Laws Calley[3]

[1]US Army Research Laboratory, 2800 Powder Mill Rd., Adelphi, Maryland 20783, USA, [2]Department of Electrical and Computer Engineering, Stony Brook University, Stony Brook, New York 11794, USA, [3]Staib Instruments, Inc., 101 Stafford Court, Williamsburg, Va 23185, USA

HgCdTe has persisted as the preferred detector material for long wavelength infrared (LWIR) applications for half a century. Its direct bandgap and long minority carrier lifetimes make it a nearly ideal material. It is, however, an expensive technology due to difficult synthesis and the need for dedicated fabrication facilities. Until recently it was assumed that no direct-bandgap III-V compound existed that could absorb light in the entire LWIR band (8-12 micron). We have demonstrated that the bandgap bowing parameter of InAsSb is such that the LWIR band can indeed be reached, and we have shown photoluminescence wavelengths up to 12.4 micron in bulk InAsSb grown without detectable alloy ordering or strain effects (Fig. 1).

Material of this type can be used in IR detector configurations with or without majority carrier blocking barrier layers. Larger bandgaps can be achieved in AlInAsSb, which can be lattice matched to LW InAsSb, albeit with a different Sb/As-ratio (Fig. 2). This allows growth of midwave absorber material and/or electron barriers. Diodes with undoped electron barriers commonly exhibit a need for significant bias to overcome unintentional internal electric fields. These are assumed to arise due to unwanted modulation doping from the barrier layer. In order to understand this process we are studying AlInAsSb layers with Al contents from 0-50%. These layers are lattice matched to InAsSb with a bandgap corresponding to 10 micron absorption.

Growth of such heterostructures requires interrupts in a MBE system with limited number of sources. This opens the possibility for undesirable composition changes or contamination of the static surface. By employing in-situ Auger electron spectroscopy enabled by the recently developed *STAIB Auger Probe* during deposition and during the static phase we can directly study composition and exchange reactions (Fig. 3). The possibility for continuous control of mixed group V alloys (As/Sb) will also be discussed.

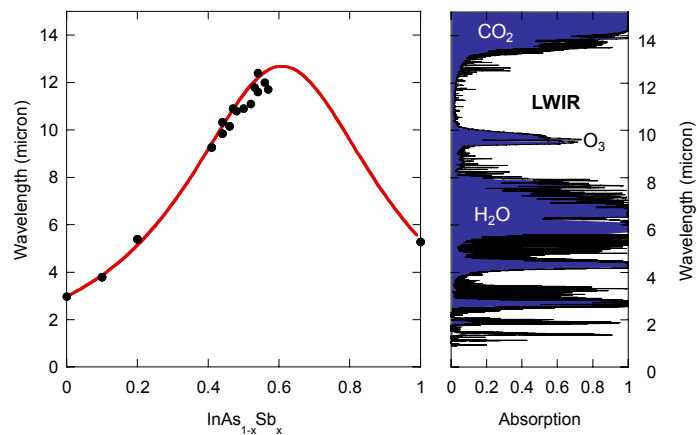©Stefan.P.Svensson.civ@mail.mil

Fig. 1. 77 K Photoluminescence from InAsSb compared with the atmospheric absorption
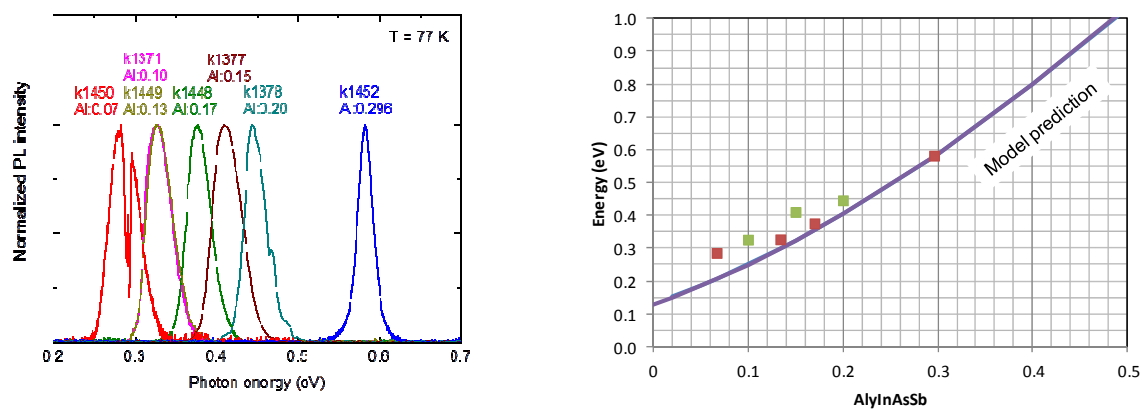

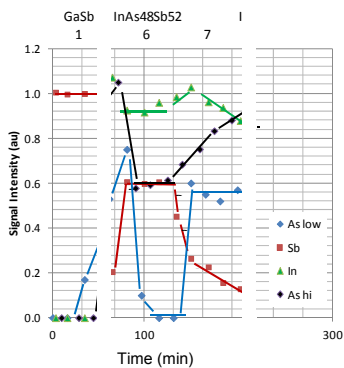Fig. 2. Photoluminescence and bandgap of AlInAsSb lattice matched to LWIR InAsSb

Fig. 3. Example of Auger electron signals from As, Sb and In during growth and interruption

Determination of N-/Ga-Rich Growth Conditions, Using In-Situ Auger Electron Spectroscopy

Stefan P. Svensson[1] Wendy L. Sarney[1], and W. Laws Calley[2]

[1]US Army Research Laboratory, 2800 Powder Mill Rd., Adelphi, Maryland 20783, USA,
[2]Staib Instruments, Inc., 101 Stafford Court, Williamsburg, Va 23185, USA

In contrast to conventional III-V MBE-growth, which is performed under group-V rich conditions, state-of-the-art GaN is grown under slightly Ga-rich conditions at very high substrate temperatures (~800 C). With this background in mind, we started growing GaNSb under Ga-rich conditions, at very low growth temperatures in order to avoid phase segregation. Surprisingly, we found that it was not possible to change the bandgap with increasing Sb-concentration following this approach [1]. Instead, the bandgap appeared to be dominated by a defect state. However, by switching to N-rich conditions, the bandgap was observed to change and roughly followed the predictions of the band-anti-crossing model [2].

These examples illustrate that determining the critical conditions where the growth changes from N- to Ga-rich is very important. The flux ratios from other III-V elements can be measured by an in-situ beam flux monitor and the fluxes for stoichiometric growth can be determined using RHEED oscillations on a single sample. However, in the case of the beam from a nitrogen source, the active N-content is usually not known and RHEED oscillations are not observed. For conventional GaN growth the typical procedure for determining the critical Ga-flux is therefore to fix the N-flow while increasing the Ga-flux. Under these conditions it may be possible to observe a change in the RHEED pattern on a single sample, but more typically a series of films are produced and the growth rate determined. Ga-rich conditions are established when the growth rate as a function of Ga-flux ceases to increase. For highly mismatched alloy (HMA) growth [1,2] this would be the only method available since the RHEED pattern does not exhibit a clear transition.

In this experiment, the N-flow was fixed to generate a steady-state background chamber pressure of 1.5×10^{-5} Torr, while the Ga source was set up to generate a linear flux ramp from 9.8×10^{16} to 3.9×10^{18} at/m^2/s over two hours. During this ramp the signals for N (375 eV), and Ga (1050 eV) were repeatedly recorded using a *STAIB Auger Probe*.

As expected, both the Ga and N signals increased as a GaN film was starting to form under N-rich conditions (grown separately and not shown here). Shortly after the start of the continued GaN growth, both the Ga and N signals started to decline and reached a steady state at around 50 minutes as shown in Fig. 1. It is unclear why this decrease in signal strength happened. Since we assume that stoichiometric material is being grown, we can speculate that it is a surface roughening effect. At about 80 min the N-signal starts decreasing, which we define as the boundary between N- and Ga-rich conditions. After this the Ga-signal exhibits a complex behavior as more and larger Ga-droplets form.
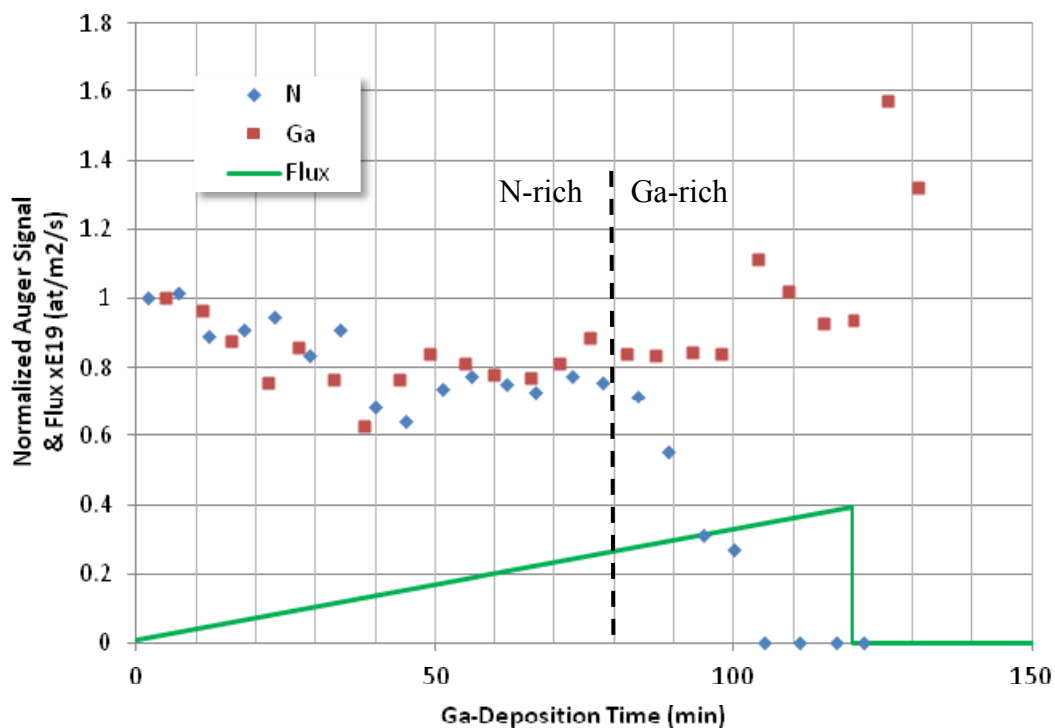
Fig. 1. Auger electron signals from Ga and N recorded as a function of time, while linearly increasing the Ga flux.

References

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